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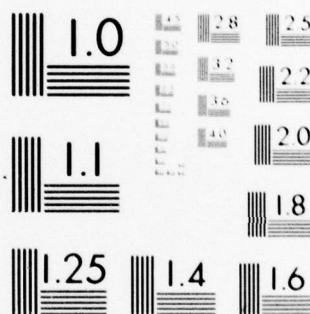
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JUL 79 J PROCHOROW, W HOPEWELL, M A EL-SAYED N00014-75-C-0602
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(10) J. Prochorow, W. Hopewell and M. A. El-Sayed

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Department of Chemistry
Los Angeles, California 90024

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THE α -SUBSTITUTION EFFECT, INTRAMOLECULAR OR MEDIUM INDUCED?

J. Prochorow,^{*} W. Hopewell and M. A. El-Sayed
Department of Chemistry
University of California
Los Angeles, California 90024

ABSTRACT

The lifetimes of ethyl- and tert-butyl benzene are measured in the gas phase and compared with one another and with those in solution. There is a large increase in the nonradiative lifetime upon going to the gas phase. Furthermore, the observed lifetime is found to be 80 nsec at low pressures, independent of the substituent, contrary to the results in solution (the α -substitution effect). These results suggest that the α -substitution effect is solvent induced.

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^{*}Permanent address: Institute of Physics, Polish Academy of Sciences,
Al. Lotnikow 32/46, 02-668 Warsaw, Poland

1. Introduction

Various substitution effects have been investigated and determined to exist from studies of the luminescence of aromatic hydrocarbon molecules [1]. In particular, a great deal of effort has been devoted to the studies of alkylbenzene molecules to investigate the effects of methyl-substitution (of the benzene molecule) on the radiative and nonradiative deactivation probabilities for the excited singlet and triplet states [2-8]. Since the very beginning, these investigations have clearly demonstrated the difficulties connected with separating the intramolecular from the intermolecular (environmental) perturbations of radiative and nonradiative decay pathways in condensed phases. This has stimulated experimental work under "collision-free" (low-pressure gas) conditions.

The possibility of the elimination of medium-assisted (intermolecular) perturbations is of great importance in all cases where the presumed "substitution effect" is believed to be connected with a modification of the intramolecular nonradiative decay channel of the excited state under consideration. For instance, it is found that in polymethylated benzenes the change from "collision-free" conditions to solution enhances only the $S_1 \rightarrow S_0$ nonradiative transition probability [9].

Among different substitution effects that were found in the series of alkylbenzenes, the " α -substitution effect" seems to be connected with particularly large changes in the nonradiative transition probability [6,10] of the lowest excited singlet state. This effect, thoroughly investigated for a series of monoalkylbenzenes (methyl-, ethyl-, isopropyl- and tert-butyl benzene) in liquid solution, was ascribed to result from an increase in the $S_1 \rightarrow S_0$ internal conversion probability with increasing the size of the alkyl group attached to the benzene ring. The magnitude of the effect is greatest

in tert-butyl benzene, for which the rate constant of internal conversion is reported to be almost one order of magnitude larger than that for toluene and almost seven times larger than that for ethyl benzene [10]. If this effect is intramolecular in nature, it would be the first experimental demonstration of a substituent changing the electronic matrix elements for the rate of the internal conversion process.

In order to distinguish between the intra- or intermolecular nature of the " α -substitution effect" we have measured the fluorescence decay times for the two most representative molecules (from the point of view of the effect under consideration), i.e., for ethyl benzene and tert-butyl benzene. Some measurements have also been performed on isopropyl benzene. The measurements for all these systems were carried out under different experimental conditions: liquid solution, saturated vapor and low pressure gas. The results show that the lifetimes are much longer in the gas phase than in solution. Furthermore, the observed lifetimes of the three compounds are found to be comparable in the gas phase at low pressure, i.e., independent of the substituent. These results suggest that the α -substitution effect is a medium induced effect. This conclusion can also explain the observation that the " α -substitution effect" is dramatically reduced when investigated in low-temperature glassy solutions [10].

2. Experimental

Commercially available (MCB) ethyl- and tert-butyl benzene were distilled and checked for purity by means of a gas chromatograph (Hewlett-Packard 5720A G.C.). Spectroquality n-hexane (MCB) was used without further purification. Gas-phase absorption spectra were recorded with the use of a Cary 14A spectrophotometer (10 cm quartz cells).

For the fluorescence measurements, solution samples were carefully deoxygenated by freeze-pump-thaw cycles (8 cycles). Gas-phase samples were prepared from deoxygenated liquids; gas being introduced to the fluorescence cell (four quartz windows at right angles) through a vacuum line. The pressure of gas was controlled and measured with the use of a thermocouple pressure gauge.

Excitation of the samples was achieved by the 266 nm fourth harmonic of a Nd/YAG laser (Quanta Ray DCR-1). The power of the laser beam was kept below 2 mJ/pulse. The emission spectra were collected by means of a Spex 0.5 m grating monochromator equipped with an optical multichannel analyzer (PARC 1205A).

Fluorescence decay times (280-282 nm) were determined with the use of a Jarrell-Ash 0.5 m grating monochromator equipped with a RCA 1P28A photomultiplier. The photomultiplier output was fed to a boxcar integrator (PAR 162-163-S5). The decay curves, recorded on a X-Y recorder, were analyzed over the first three lifetimes by taking the log of the intensity vs. time and fitting the points with a least-squares program. Decay times obtained from different measurements, at the same pressure (2-3 samples), were all within ± 3 ns of each other. No wavelength dependence of the decay time was observed. Calibration of the detection system was performed with fluoranthene in cyclohexane solution, for which the decay time of fluorescence was found to be 51 ns (as compared to 53 ns reported in the literature [11]).

3. Results

The gas-phase absorption and fluorescence spectra of the compounds are shifted toward higher energies by ~ 30 nm from the solution spectra in n-hexane [11]. The fluorescence spectrum has more pronounced vibrational

structure on going from solution to the gas phase. However, no significant changes are observed in either the wavelength or the structure of the spectrum at different gas pressures.

The fluorescence decay times for different experimental conditions are summarized in Table 1. It is seen that in solution, decay times for both compounds have values close to that obtained in previous work (35.2 ns [10] or 31 ns [11] for ethyl benzene and 10 ns [10] for tert-butyl benzene) and that the decay time of t-butyl benzene is approximately one-third that of ethyl benzene.

Upon going to the gas phase, both compounds are found to have a much longer observed lifetime than that in solution (by a factor of 2-3 for ethyl benzene and 6-7 for the tert-butyl). Furthermore, the large difference in lifetime between the two compounds vanishes in the gas phase. At pressures of 0.1 torr or lower both compounds are found to have a lifetime of ~ 80 nsec. Similar behavior is observed also for isopropyl benzene. Its lifetime is found to be 58 nsec at its saturated vapor pressure but is increased to 80 nsec at 6.5×10^{-2} torr. In all these measurements, the decay seems to be exponential over \sim three lifetimes.

4. Discussion

The above results can be summarized as follows. In solution, the observed lifetime of ethyl benzene is 300% longer than that for t-butyl benzene. In the gas phase, however, the lifetime of both compounds is increased by $>200\%$ for ethyl benzene and by $>600\%$ for t-butyl benzene. Equally important, the large difference in their lifetime disappears. The observed lifetime increases slowly as the pressure is decreased and becomes ~ 80 nsec at 0.10 torr or lower pressures, independent of the substituent. Thus upon going from the solution to the gas phase a large increase in the observed lifetime is found as well as a large decrease in the sensitivity of the lifetime to the type of

substituent. These observations can be due to changes in the radiative or nonradiative probability upon going to the gas phase. Large changes in the radiative lifetime can be examined by comparing the absorption spectra in the gas and in solution. This has been carried out and the value of $\epsilon_{\max} (\text{M}^{-1} \text{cm}^{-1})$ for solution is found to be ~ 250 for ethyl and ~ 200 for t-butyl benzene and that in the gas phase is found to be ~ 200 and ~ 250 for ethyl and t-butyl benzene, respectively. The Franck-Condon envelope of the spectrum does not change in the two phases. These observations strongly suggest that the 300-600% increase in the observed lifetime upon changing to the gas phase is due to changes in the nonradiative probability which increases greatly in solution. This further suggests that the observed sensitivity of these processes to substituent in solution gives rise to the observed α -substituent effect. This sensitivity as well as the nonradiative processes themselves in solution must then be medium induced, e.g., resulting from solvent-solute collision induced nonradiative (e.g., $S_0 \leftarrow S_1$) processes (as was found for polymethylated benzenes [9]) or from reversible or irreversible solvent-solute photochemistry.

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Table 1. Decay times of fluorescence, τ (± 3 ns), of ethylbenzene and tert-butylbenzene measured at different experimental conditions

Compound Conditions	Ethylbenzene	t-Butylbenzene
	τ , ns	τ , ns
Solution *	31	11
Saturated vapor	53	60
Gas ($p = 0.1$ torr)	80	75
Gas ($p = 4 \times 10^{-2}$ torr)	81	75

* n-hexane solution, 2×10^{-3} M concentration

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